

## RESEARCH PAPER RP1144

Part of Journal of Research of the National Bureau of Standards, Volume 21,  
November 1938

# HYDROGENATION OF THE "EXTRACT" PORTION OF THE LUBRICANT FRACTION FROM A MIDCONTINENT PETROLEUM<sup>1</sup> \*

By Beveridge J. Mair, Charles B. Willingham, and Anton J. Streiff<sup>2</sup>

## ABSTRACT

To obtain information about the chemical constitution of the extract portion of the lubricant fraction from a midcontinent petroleum, fifteen selected fractions, prepared by extensive distillation and extraction, were completely hydrogenated. The hydrogenation procedure is described and there are tabulated and compared values for the physical constants of the fractions before and after hydrogenation. Evidence is presented to show that, under the conditions of these experiments, namely, temperatures from 230° to 250° C and pressures of hydrogen from 170 to 210 atm, the fractions were completely hydrogenated and that no break-down of the molecules occurred.

## CONTENTS

	Page
I. Introduction.....	565
II. Hydrogenation equipment.....	567
III. Preliminary hydrogenation experiments and catalysts used.....	567
IV. Hydrogenation procedure.....	570
V. Determination of physical properties.....	571
VI. Discussion of results.....	571
1. Molecular weight.....	575
2. Specific refractive dispersion.....	576
3. Specific refraction.....	576
4. Silica gel experiments.....	578
5. Aniline point.....	580
VII. Conclusion.....	580
VIII. References.....	580

## I. INTRODUCTION

That hydrogenation is a powerful tool for investigating the chemical composition of lubricating oil fractions has been demonstrated by Vlugter, Waterman, and Van Westen [1].<sup>3</sup> More recently the method has been used by Müller and Neyman-Pilat [2]. By controlled hydrogenation, these authors convert practically completely the aromatic rings into hydroaromatic or naphthenic rings, without breaking down the molecule. By measuring the hydrogen consumed in the

<sup>1</sup> Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

<sup>2</sup> Research Associates at the National Bureau of Standards, representing the American Petroleum Institute.

<sup>3</sup> Figures in brackets indicate the literature references at the end of this paper.

\* This paper was originally presented before the Petroleum Division of the American Chemical Society at Milwaukee on September 8, 1938.

process, or by determining the  $x$  value in the formula  $C_nH_{2n+x}$  before and after hydrogenation, it is possible with certain reasonable assumptions to compute the average number of aromatic rings in the original fraction.

In an investigation [3] of the composition of the extract portion of the lubricant fraction from a midcontinent petroleum, there were prepared in this laboratory five series of fractions which are believed to be more nearly homogeneous with respect to size and type of molecule than any fractions hitherto obtained from the extract portion of the lubricant fraction of any petroleum.

The source of these fractions is shown graphically in figure 1. They were prepared from the extract portion of the lubricant fraction

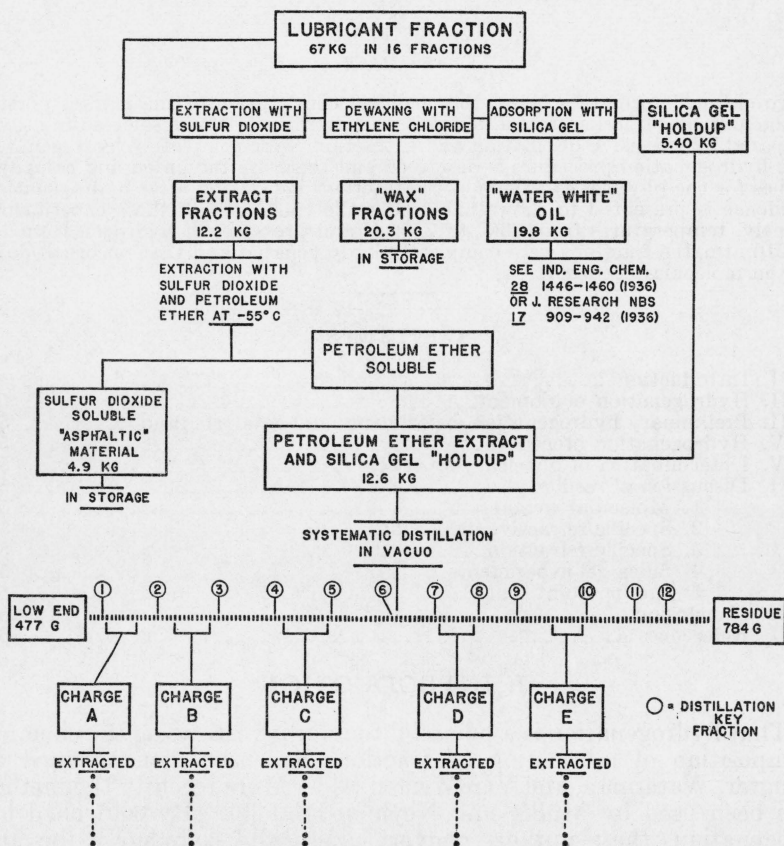


FIGURE 1.—Chart showing treatment and disposition of lubricating-oil fractions.

of a midcontinent petroleum by extensive distillation followed by the exhaustive extraction of charges with narrow-boiling ranges in 16.7-m columns, using methyl cyanide or a mixture of methyl cyanide and acetone as a solvent. In correlating the large number of physical data which had been obtained on these extraction fractions, it became evident that a direct determination of the number of aromatic rings per molecule by the hydrogenation method would be of great value

in interpreting the physical properties of these fractions in terms of their chemical constitution. Furthermore, the hydrogenation process would yield naphthenic fractions with several rings per molecule whose physical properties would also be of value in this correlation.

This paper describes the method employed in hydrogenating 15 of these extraction fractions and tabulates for comparison the physical properties of the fractions before and after hydrogenation. The fractions which were hydrogenated resulted from the extraction of series *B*, *C*, and *E* (fig. 1). Their position in the extraction series is recorded in table 2.

## II. HYDROGENATION EQUIPMENT

Hydrogenation equipment, complete with bomb with thermocouple well, heating and shaking devices, and gages similar to that described by Adkins [4] was used.<sup>4</sup> The volumes of the bomb and copper liner were 500 and 350 ml, respectively. Two hydrogen cylinders were used. The bomb was first charged by the more nearly exhausted cylinder and finally by a full or nearly full cylinder, so that the initial pressure at room temperature was always above 100 atm.

## III. PRELIMINARY HYDROGENATION EXPERIMENTS AND CATALYSTS USED

The experience gained in the preliminary experiments, the results of which are recorded in table 1, determined the procedure adopted. These experiments were performed at temperatures of 230° to 250° C and at pressures of from 170 to 210 atm of hydrogen and the time of each treatment was from 10 to 12 hours. It should be noted that the fractions contained considerable quantities of sulfur and oxygen and one contained 0.71 percent of nitrogen.

<sup>4</sup> This equipment was purchased from the American Instrument Co., Silver Spring, Md.

TABLE 1.—*Results of experiments in the hydrogenation of oil fractions*  
 (Temperatures, 230° to 250° C; hydrogen pressure, 170 to 210 atm; time per hydrogenation, 10 to 12 hours)

Catalyst <sup>a</sup>	Number of treatments with hydrogen	Refractive index $n_D^{25}$	Refractive dispersion $n_D - n_C$ at 25° C	Sulfur <sup>b</sup> content	Nitrogen <sup>b</sup> content	Oxygen <sup>b</sup> content	Remarks	Solvent and amount used
FRACTION C-20 (14 g)								
<i>g</i>				Percent by wt (0.0)	Percent by wt (0.01)	Percent by wt (0.53)		<i>ml</i>
3 Ni-K	0	1.5622	0.0183	-----	-----	-----	-----	None.
3 Ni-K	1	1.5571	.0178	-----	-----	-----	-----	Do.
3 Ni-K	2	1.5470	.0158	-----	-----	-----	-----	Do.
3 Ni-K	3	1.5402	-----	-----	-----	-----	-----	Do.
3 Ni-K	4	1.5369	.0139	-----	-----	-----	-----	Do.
10 Ni-K	5	1.5295	.0130	-----	-----	-----	-----	75— <i>n</i> -heptane.
10 Ni-K	6	1.5084	.0103	-----	-----	-----	-----	Do.
10 Ni-K	7	1.5005	.0092	-----	-----	-----	-----	Do.
FRACTION C-13 (17 g)								
-----	0	1.5911	0.0234	(1.4)	(0.02)	(0.7)	-----	-----
10 Ni-K	1	1.5762	.0209	-----	-----	-----	NiS formed	75— <i>n</i> -heptane.
7 Ni-R	2	1.5554	.0170	-----	-----	-----	do.	Do.
15 Ni-R	3	1.5201	.0113	-----	-----	-----	do.	Do.
15 Ni-R	4	1.5062	.0066	-----	-----	-----	do.	Do.
15 Ni-R	5	1.5047	.0062	-----	-----	-----	Trace of NiS formed	Do.



## FRACTION C-7 (20 g)

	0	1. 6189	(0. 0281)	(1. 5)	(0. 05)	(0. 8)		
50 Ni-R	1	1. 5442	. 0142	-----	-----	-----	NiS formed	75— <i>n</i> -heptane.
45 Ni-R	2	1. 5228	. 0113	-----	-----	-----	No NiS formed	75—methylcyclohexane.
40 Ni-R	3	1. 5175	. 0106	-----	-----	-----	do.	Do.
30 Ni-R	4	1. 5079	. 0097	-----	-----	-----	do.	Do.
25 Ni-R	5	1. 5059	. 0093	-----	-----	-----	do.	Do.

## FRACTION E-1 (32 g)

	0	(1. 63)	(0. 030)	0. 81	0. 71	1. 46		
45 Ni-R	1	1. 5677	-----	-----	-----	-----	Ammonia formed	75—methylcyclohexane.
45 Ni-R	2	1. 5348	. 0127	-----	-----	-----	do.	Do.
45 Ni-R	3	1. 5218	. 0110	-----	-----	-----	do.	Do.
40 Ni-R	4	1. 5189	. 0106	-----	-----	-----	do.	Do.
45 Ni-R	5	1. 5162	. 0103	-----	-----	-----	do.	Do.
40 Ni-R	6	1. 5138	. 0101	-----	-----	-----	do.	Do.
40 Ni-R	7	1. 5122	. 0100	-----	-----	-----	Trace of ammonia formed	Do.
45 Ni-R	8	1. 5109	. 0098	-----	-----	-----	-----	Do.
45 Ni-R	9	1. 5100	. 0097	-----	-----	-----	-----	Do.
45 Ni-R	10	1. 5096	. 0097	-----	-----	-----	-----	Do.

<sup>a</sup> Ni-K is nickel on kieselguhr; Ni-R is Raney nickel.

<sup>b</sup> Values in parentheses were estimated.

The catalyst used in the first experiment on fraction *C-20* (wt about 14 g) was nickel-on-kieselguhr, prepared as described by Adkins [4]. The hydrogenation of acetone with this catalyst was found to proceed readily and at about the rate reported by Adkins. Naphthalene also was readily hydrogenated to decahydronaphthalene. Seven treatments using 3- and 10-g portions of catalyst were required before fraction *C-20* was free from nonnaphthenic material.

In the second experiment, with fraction *C-13*, the catalyst recovered from each treatment was tested for NiS, which was found up to the fourth treatment, with a trace in the fifth. A total of 10 g of nickel-on-kieselguhr and 52 g of Raney<sup>5</sup> nickel was used in this experiment.

In the next experiment with fraction *C-7*, which contained 1.5 percent of sulfur, 50 g of Raney nickel in the first treatment was sufficient to remove the sulfur completely. It is evident, at least during the first treatment of these oils with high sulfur content, that a large quantity of catalyst (50 g catalyst for 20 g of oil) is advantageous.

The experiment with fraction *E-1* is included in table 1 because in addition to its high sulfur content this oil contained 0.71 percent of nitrogen. The solution of oil in solvent smelled strongly of ammonia after each treatment from the second to the sixth, and a faint ammoniacal odor could be detected after the seventh treatment. It is probable that ammonia was present after the first treatment but was overlooked. This fraction was treated 10 times and in the final stages the hydrogenation progressed extremely slowly.

Since there seemed to be no advantage in the use of nickel-on-kieselguhr, Raney nickel was used in all experiments except the first and part of the second. One hydrogenation treatment was made with Raney nickel produced from the commercial alloy, as described by Adkins [4]. The results of this treatment were in no way superior to those obtained with the commercial catalyst preserved in water which was used in the remainder of the experiments. Solvent was necessary on account of the large ratio of catalyst to oil.

#### IV. HYDROGENATION PROCEDURE

The procedure finally adopted in the hydrogenation treatments was as follows: The oil fraction (12 to 30 g) was dissolved in 75 ml of methylcyclohexane and transferred to the liner. About 40 to 50 g of Raney nickel which was stored under water was transferred to a sintered glass filter and most of the water drawn off by suction. It was then washed with alcohol and finally with methylcyclohexane, and transferred while still wet to the liner, which was previously filled with carbon dioxide.

After each hydrogenation treatment of from 10 to 12 hours at 230° to 250° C, the oil and solvent were separated from the catalyst with the use of a sintered-glass filter, and the catalyst was washed with more methylcyclohexane. The refractive index and refractive dispersion were determined on a small portion of the oil from which the solvent had been removed by heating in vacuum. After removal by

<sup>5</sup> Raney nickel, a product developed by Murray Raney, was purchased from the Gilman Paint and Varnish Co., of Chattanooga, Tenn. This catalyst is prepared from a finely ground nickel-aluminum alloy by dissolving the aluminum with sodium hydroxide solution.

distillation of the extra solvent used in washing, the oil was ready for the next treatment with a fresh portion of catalyst. After the final treatment, the solvent was removed from the oil by distillation and finally by sweeping out at 110° C at a low pressure (25 mm) with carbon dioxide.

The loss of oil in a complete hydrogenation was usually from 2 to 4 g (about 10 to 20 percent), about 1 g of which could be accounted for as adhering to the walls of the vessel in which the sample was freed from solvent. The oil became water-white after the first treatment.

Hydrogenation treatments on any fraction were continued until the specific dispersion,  $(n_F - n_C)/d \times 10^4$ , decreased to about 100, a value (discussed later) characteristic of naphthenes.

## V. DETERMINATION OF PHYSICAL PROPERTIES

The same methods were employed in determining the physical properties of the hydrogenated fractions as were employed in determining their properties before hydrogenation. These methods have been described elsewhere [3].

## VI. DISCUSSION OF RESULTS

The physical properties of the fractions before and after hydrogenation are recorded in table 2. That there has been a fundamental change in most of the physical properties is obvious. Since a detailed discussion of these properties will be given in a subsequent paper, only the more obvious differences will be pointed out here.

TABLE 2.—Physical properties of hydrogenated and unhydrogenated fractions

Fraction	Percentage extracted	Number of treatments with hydrogen	Kinematic viscosity at—		Kinematic-viscosity index *	Refractive index <sup>b</sup> $n_D^{25}$	Density <sup>c</sup> at 25° C	Refractive dispersion $n_F - n_C$ at 25° C	Specific optical rotation $[\alpha]_D^{25}$	Aniline point	Specific refraction $\frac{n^2-1}{n^2+2} \times \frac{1}{d}$	Specific dispersion <sup>d</sup> $\frac{n_F - n_C}{d}$
			100° F	210° F								
			<i>Stokes</i>	<i>Stokes</i>			<i>g/ml</i>			° C		
B-12.....	33.7 to 36.4		12.0	0.150	—560	1.5952	1.030	0.0236			0.3299	0.0229
B-12-H.....		4	1.37	0.0740	—143	1.5000	0.9291	.0093		84.0	.3166	.0100
B-16.....	44.5 to 47.2		8.31	.144	—369	1.5785	1.010	.0207	(0.42)	—3.5	.3287	.0205
B-16-H.....		5	1.49	.0791	—124	1.5000	0.9272	.0093	.19	85.8	.3173	.0100
B-19.....	52.4 to 54.8		5.60	.130	—269	1.5652	.9942	.0187	(.67)	(6.9)	.3277	.0188
B-19-H.....		4	1.42	.0809	—91	1.4991	.9244	.0093	.30	87.8	.3177	.0101
C-1 <sup>a</sup> .....	0 to 5.2		(300)*	.340	(—3,500)*	(1.641)	1.076	(.032)	(.05)*		.3353	(.030)*
C-1-H.....		8	2.79	.0907	—284	1.5044	0.9381	.0094	.03	82.4	.3159	.0100
C-7.....	20.6 to 23.9		70.3	.253	—1,340	1.6189	(1.05)	(.0281)	(.27)		(.333)	(.0267)
C-7-H.....		5	3.67	.107	—254	1.5059	0.9417	.0093	.15	82.4	.3154	.0099
C-13.....	37.3 to 39.9		29.8	.229	—606	1.5911	1.025	.0234	(.50)		.3298	.0228
C-13-H.....		5	4.16	.121	—199	1.5047	0.9389	.0092	.19	84.9	.3157	.0098
C-20.....	55.0 to 57.2		9.87	.182	—223	1.5622	.9909	(.0183)	(.83)	14.4	.3274	(.0185)
C-20-H.....		7	2.70	.112	—96	1.5005	.9280	.0092	.31	90.6	.3172	.0099
C-(26+27).....	66.7 to 70.3		(2.95)	(.125)	(—61)	(1.5325)	(.956)	(.0140)	(1.14)	(35.7)	(.3245)	(.0147)
C-(26+27)-H.....		5	1.78	.102	—27	1.4947	.9136	.0090	0.48	96.9	.3190	.0099
C-30.....	74.1 to 75.9		1.72	.103	—14	1.5215	.9403	.0125	(.89)	44.2	.3241	.0133
C-30-H.....		2	1.30	.0912	+1	1.4909	.9047	.0090	.42	98.9	.3201	.0099
C-33.....	80.3 to 82.5		1.01	.0806	+8	1.5111	.9230	.0117	(.69)	(50.6)	.3246	.0127
C-33-H.....		2	0.898	.0809	+37	1.4868	.8944	.0089	.28	101.2	.3215	.0100
C-35.....	84.5 to 86.7		.738	.0752	+53	1.5056	.9124	.0112	(.41)	55.9	.3254	.0123
C-35-H.....		2	.687	.0718	+51	1.4823	.8837	.0088	.19	104.0	.3228	.0100
C-37.....	88.9 to 91.2		.570	.0674	+69	1.4993	.8996	.0106	.38	62.4	.3266	.0118
C-37-H.....		1	.586	.0691	+72	1.4799	.8755	.0087	.38	105.4	.3244	.0099
C-res.....	96.3 to 100		.364	.0579	+112	1.4711	.8560	.0082	.81	111.1	.3266	.0096
C-res.-H.....		1	.395	.0571	+107	1.4707	.8552	.0084	.82	112.3	.3267	.0098
E-1 <sup>a</sup> .....	0 to 8.8		(>1,000)*	(>1.8)*	(<—2,000)*	(1.63)*	1.074	(.030)*			(.334)*	(.028)*
E-1-H.....		10	48.8	.282	—671	1.5096	0.9466	.0097		90.4	.3158	.0102
E-25.....	72.6 to 75.3		4.51	.187	+10	1.5210	(.943)	(.0124)	(.92)	(57.3)	(.3238)	(.0132)
E-25-H.....		4	3.11	.155	+19	1.4920	.9047	.0092		109.1	.3207	.0102



Fraction	Boiling point at 1mm Hg	Mole- cular weight	Combustion analyses		Sulfur content	Nitrogen content	Oxygen content	In the formula $C_nH_{2n+2}S_yN_zO_w$				
			Ratio moles $H_2O/CO_2$	Mass of sample less mass of C+H				<i>n</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>w</i>
B-12.....	° C (202)	(308)	(0.604)	(2.36)				(22.7)	(-18.00)			
B-12-H.....	169	314	.8747	0.06				22.8	-5.71			
B-16.....	(202)	(318)	(.656)	(1.78)				(23.4)	(-16.10)			
B-16-H.....	176	324	.8777	0.07				23.5	-5.74			
B-19.....	(202)	(326)	(.682)	(1.26)				(24.1)	(-15.35)			
B-19-H.....	179	329	.8827	0.08				23.9	-5.60			
C-1.....	218	303	.5363	2.63	0.77	0.56	1.30	22.5	-20.90	0.07	0.12	0.25
C-1-H.....	168	309	.8676	0.08				22.5	-5.95	.0	.0	.0
C-7.....	(217)	(318)	(.581)	(2.38)	(1.53)	(.05)	(0.80)	(23.5)	(-19.70)	(.15)	(.01)	(.16)
C-7-H.....	179	329	.8655	0.16				23.5	-6.33	.0	.0	.0
C-13.....	(217)	(330)	(.637)	(2.12)	(1.40)	(.02)	(.70)	(24.4)	(-17.72)	(.14)	(.00)	(.14)
C-13-H.....	188	341	.8686	0.16				24.7	-6.49	.0	.0	.0
C-20.....	(217)	(347)	(.696)	(1.45)	(0.90)	(.01)	(.53)	(25.5)	(-15.50)	(.10)	(.00)	(.11)
C-20-H.....	197	353	.8807	0.03				25.6	-6.11	.0	.0	.0
C-(26K27).....	(216)	(372)	(.759)	(1.0)	(.50)	(.01)	(.49)	(27.2)	(-13.10)	(.06)	(.00)	(.11)
C-(26K27)-H.....	204	376	.8977	0.04				27.2	-5.57	.0	.0	.0
C-30.....	(215)	(384)	(.794)	(.73)	(.36)	(.01)	(.36)	(28.0)	(-11.55)	(.04)	(.00)	(.09)
C-30-H.....	208	384	.9086	.04				27.7	-5.07	.0	.0	.0
C-33.....	(215)	(390)	(.814)	(.64)	(.34)	(.00)	(.30)	(28.4)	(-10.56)	(.04)	(.00)	(.07)
C-33-H.....	210	393	.9215	.02				28.3	-4.45	.0	.0	.0
C-35.....	(216)	(393)	(.829)	(.70)	(.36)	(.00)	(.34)	(28.5)	(-9.75)	(.04)	(.00)	(.08)
C-35-H.....	212	396	.9314	.08				28.5	-3.91	.0	.0	.0
C-37.....	(216)	(401)	(.852)	(.60)	(.30)	(.00)	(.30)	(29.0)	(-8.6)	(.04)	(.00)	(.07)
C-37-H.....	216	402	.9436	.03				28.9	-3.26	.0	.0	.0

See footnotes at end of table.



TABLE 2.—Physical properties of hydrogenated and unhydrogenated fractions—Continued

Fraction	Boiling point at 1 mm Hg	Molecular weight	Combustion analyses		Sulfur content	Nitrogen content	Oxygen content	In the formula $C_nH_{1n+z}S_xN_yO_w$				
			Ratio moles $H_2O/CO_2$	Mass of sample less mass of C+H				<i>n</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>w</i>
	° C			Percent by wt	Percent by wt	Percent by wt	Percent by wt					
<i>C-res.</i> .....	219	420	.9696	.02				30.1	-1.85	(.00)	(.00)	(.00)
<i>C-res.-H.</i> .....	220	417	.9716	.04				29.9	-1.69	.0	.0	.0
<i>E-1</i> <sup>a</sup> .....	(256)	367	.5666	2.98	.81	.71	1.46	27.1	-23.46	.09	.19	.33
<i>E-1-H</i> .....	207	367	.8639	0.06				26.7	-7.26	.0	.0	.0
<i>E-25</i> .....	(256)	(456)		(.6)	(.34)	(.01)	(.25)	33.1	(-11.7)	(.05)	(.00)	(.07)
<i>E-25-H</i> .....	247	455	.9141	.06				32.8	-5.64	.0	.0	.0

<sup>a</sup> Values in parentheses were estimated by interpolation or extrapolation. Those with an asterisk (\*) are rough estimates.

<sup>b</sup> The values of the refractive index may be converted to other temperatures by using for  $dn_D/dt$  the value 0.00035 per ° C. Over a 5-degree temperature interval, this conversion will not introduce an uncertainty greater than  $\pm 0.0002$ .

<sup>c</sup> The values of the density may be converted to other temperatures by using for  $dD/dt$  the value 0.0007 g/ml per ° C. Over a 5-degree interval, this conversion will not introduce an uncertainty greater than  $\pm 0.0003$  g/ml.

<sup>d</sup> The values for the specific refraction and specific dispersion may be regarded as constant over a 5-degree range of temperature within the accuracy of these measurements.

<sup>e</sup> Kinematic-viscosity indices were computed with the aid of the tables given by Hersh, Fisher, and Fenske [5].

The change in physical properties on hydrogenation is very pronounced for the first fraction extracted, and is almost negligible for the residue. For the first fractions extracted, there is on hydrogenation a great decrease in viscosity and a marked increase in viscosity index. The refractive index, density, refractive dispersion, specific refractive dispersion, specific optical rotation, and specific refraction decrease pronouncedly. The aniline point increases and the boiling point decreases. There is a slight increase in molecular weight. The number of carbon atoms per molecule, however, remains constant. The results of the combustion analyses show, of course, an increase in the ratio of hydrogen to carbon. They show also that the sulfur, nitrogen, and oxygen (except for a trace) have been removed by the hydrogenation process.

For the purpose for which the data on the hydrogenated fractions are to be employed, it is important to know that there has been no loss of carbon atoms in the hydrogenation process and that after hydrogenation the fractions are substantially free from nonnaphthenic material.

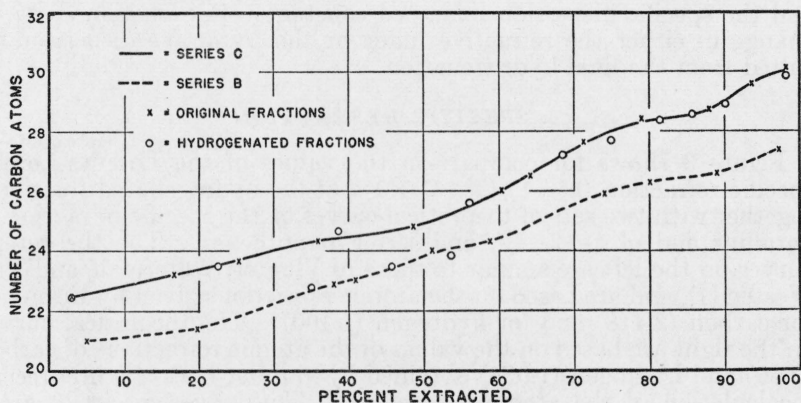


FIGURE 2.—Number of carbon atoms per molecule for the fractions from extractors B and C, before and after hydrogenation.

### 1. MOLECULAR WEIGHT

In figure 2 the number of carbon atoms per molecule, both for the original fractions from two series (B and C) and for the fractions after hydrogenation, is plotted with respect to the percentage extracted. It is apparent that the points fall close to smooth curves, and that the number of carbon atoms per molecule for the hydrogenated fractions, as estimated from the curves, does not differ by more than about 0.2 carbon atom from that experimentally determined. This is within the limits of accuracy of the molecular-weight determinations, and it may be concluded that there has been no loss of carbon atoms in the hydrogenation process.

From a consideration of the specific refractive dispersions, specific refractions, and the behavior of the fractions on treatment with silica gel, it is possible to ascertain whether these fractions are substantially free from aromatic hydrocarbons.

## 2. SPECIFIC REFRACTIVE DISPERSION

Vlugter, Waterman, and Van Westen [6] have pointed out that an oil is practically free from aromatic hydrocarbons when the specific dispersion,  $(n_g - n_c)/d \times 10^4$ , is less than 158. Von Fuchs and Anderson [7] found, in a review of dispersion data for synthetic hydrocarbons, principally those of low molecular weight, that the values for the specific dispersion,  $(n_F - n_C)/d \times 10^4$ , of naphthenes and paraffins lie in the region 95 to 102—the average value for the naphthenes being 98.3 and that for paraffins 98.4. Five of the six 1- and 2-ring naphthene hydrocarbons of high molecular weight synthesized by Mikeska [7] have specific dispersions,  $(n_F - n_C)/d \times 10^4$ , between 97 and 100, and confirm the observation of Von Fuchs and Anderson [7]. It is apparent that if fractions have specific dispersions  $\times 10^4$  of 100 or less they contain little, if any, aromatic hydrocarbons.

Of the 15 fractions hydrogenated, 12 have specific refractions of 100 or less. For the two fractions *E-1* and *E-25*, specific dispersions of 102 were obtained. On the last hydrogenation treatment of *E-1*, the refractive index changed by only four units in the fourth decimal place, and the specific dispersion remained constant. For fraction *E-25* no change in either the refractive index or the refractive dispersion resulted from the final hydrogenation.

## 3. SPECIFIC REFRACTION

Figure 3 shows for comparison the values of the Lorentz-Lorenz specific refraction  $(n^2 - 1)/(n^2 + 2) \times 1/d$  of the hydrogenated fractions, together with two sets of theoretical curves of the specific refraction of paraffins and of 1-, 2-, 3-, and 4-ring naphthenes. The theoretical curves on the left are similar to those of Vlugter, Waterman, and Van Westen [1], and are based on the atomic refractions given by Eisenlohr for carbon (2.418) and for hydrogen (1.100). The theoretical curves on the right are based on the values of the atomic refractions of carbon (2.59) and hydrogen (1.025) obtained by van der Hulst [9] in a recent recalculation of the atomic refractions. The values in circles are  $x$  values in the expression  $C_nH_{2n+x}$  obtained for the hydrogenated fractions. The values in squares are the  $x$  values of fractions of "water-white" oil obtained by extraction and described elsewhere [10]. Only those fractions of water-white oil whose specific dispersions,  $(n_F - n_C)/d \times 10^4$ , were 100 or lower have been plotted.

It is evident that there is a very considerable difference in the position of the two sets of theoretical curves, and that the values for the specific refractions of the oil fractions are all much too low to correspond with the curves based on van der Hulst's values. The specific refractions of most of the water-white oil fractions are in good agreement with the curves based on Eisenlohr's values. The specific refractions of the hydrogenated fractions are a little too high and lie between the two sets of curves. Waterman and Leendertse [11] also have found that the specific refractions of a series of oils prepared by complete hydrogenation of mineral oils and of polymerized olefins were much too low to agree with van der Hulst's values and a little too high to agree with Eisenlohr's values. Since both our values and those of Waterman and Leendertse are in much better agreement with Eisenlohr's values, and since refraction values higher but not

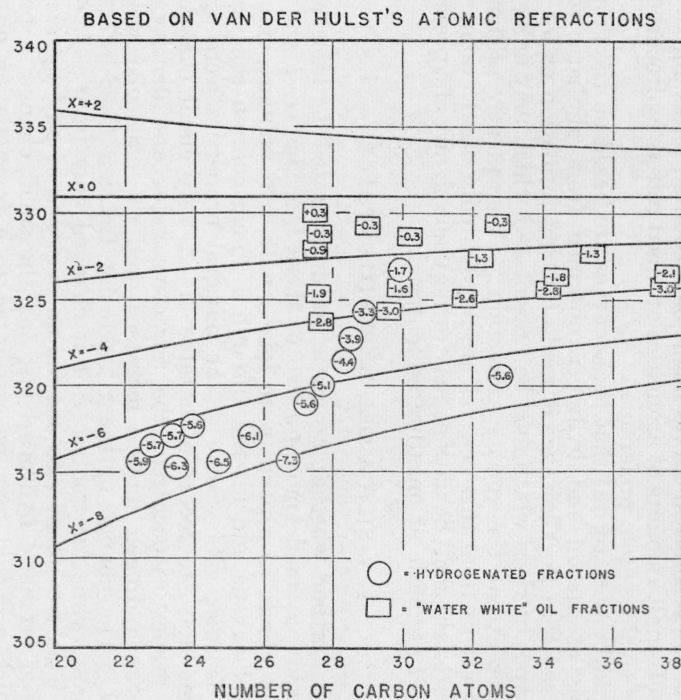
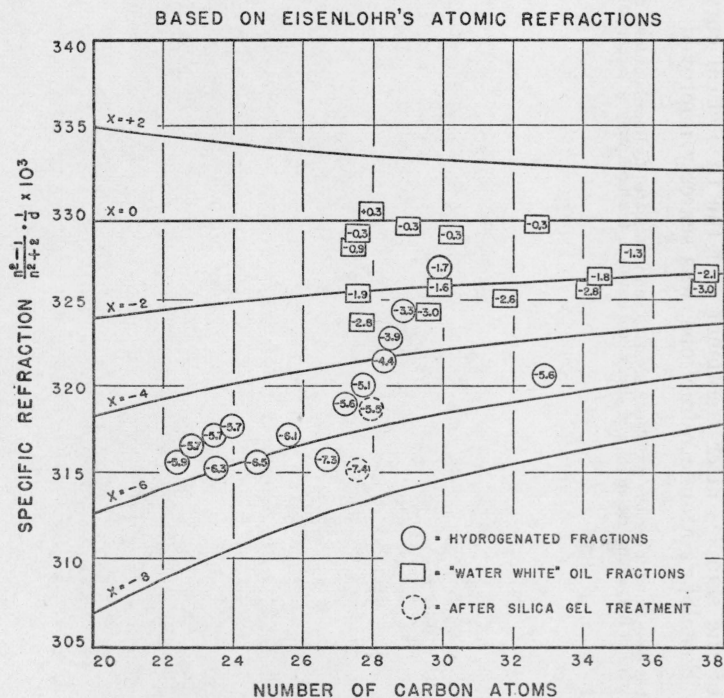


FIGURE 3.—Specific refractions of hydrogenated and of water-white oil fractions compared with theoretical curves for the specific refractions.

The curves at the left are based on Eisenlohr's atomic refractions; those on the right are based on van der Hulst's atomic refractions.



lower than the theoretical curves might be accounted for as due to the presence of small amounts of aromatics or unsaturated hydrocarbons, Eisenlohr's values seem preferable.

It should be pointed out that these curves are based on the atomic refractions of carbon and hydrogen obtained from aliphatic compounds, and that no allowance is made for ring formation or for the various types of rings which may be present and which may influence to a minor extent the specific refraction. Consequently, although gross deviations from these curves are undoubtedly due to nonnaphthenic material, small deviations may or may not signify the presence of traces of aromatic or unsaturated material.

#### 4. SILICA GEL EXPERIMENTS

To test further whether aromatic or unsaturated hydrocarbons were present in small amounts, two of these fractions, *E-1* and *C-26+27*, of about 15 g each, were mixed with two volumes of pure methylcyclohexane and filtered through a 30-cm column containing 5 g of fine silica gel.<sup>6</sup> Some of the physical properties were again determined and are recorded in table 3. A very small change in physical properties occurred; the refractive index and density decreased, the hydrogen content increased, and the molecular weight increased. The change in the  $x$  value for fraction *C-26+27* was insignificant, while for fraction *E-1* it changed only from  $-7.26$  to  $-7.40$ . This treatment also showed no evidence of any significant quantity of aromatic hydrocarbons, and the small change in properties which occurred may be attributed to a fractionation on the basis of molecular weight. The agreement between the specific refraction of the samples after treatment and the theoretical curves, based on Eisenlohr's atomic refractions, was scarcely improved.

<sup>6</sup> Silica gel has been found to remove completely aromatic and unsaturated hydrocarbons from naphthenes or paraffins in the gasoline region [12] and also, where tested, in the lubricating oil region [13].



TABLE 3.—Physical properties of hydrogenated fractions before and after silica gel treatment

Fraction	Refractive index $n_D^{25}$	Refractive dispersion $n_F - n_C$ at 25° C	Density at 25° C	Specific refractive dispersion $\frac{n_F - n_C}{d}$	Specific refraction $\frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d}$	Molecular weight	Combustion analyses		In the formula $C_nH_{1.7n+2}$	
							Ratio: moles $H_2O/CO_2$	Mass of sample less mass of C+H	n	x
C-26+27 { Before..... After.....	1.4947	0.0090 <sub>6</sub>	<i>g/ml</i> 0.9136	0.0099	0.3190	376	0.8977	<i>Percent by wt.</i> 0.04	27.2	-5.57
	1.4936	.0090 <sub>8</sub>	.9128	.0099	.3187	386	.9009	.05	27.9	-5.53
E-1 { Before..... After.....	1.5096	.0097 <sub>4</sub>	.9466	.0102	.3158	367	.8639	.06	26.7	-7.26
	1.5082	.0097 <sub>7</sub>	.9464	.0103	.3151	378	.8653	.06	27.5	-7.40

## 5. ANILINE POINT

Since Vlugter, Waterman, and Van Westen [1] give a series of curves showing the relationship between aniline points and specific refractions for hydrogenated fractions of different molecular weights, a comparison is possible between the aniline points found by them and those found in this investigation. In table 4 are compared the aniline points of fractions with the same molecular weight and specific refraction. In some instances, the values found in this investigation are higher and in some instances lower than those found by Vlugter, Waterman, and Van Westen, but considering the fact that the comparison involves not only the determination of aniline points but also of molecular weight, refractive index, and density, the agreement is good.

TABLE 4.—*Aniline points of hydrogenated fractions compared with those of Vlugter, Waterman, and Van Westen*

Fraction	Aniline points		Fraction	Aniline points	
	This work	Vlugter, Waterman, and Van Westen		This work	Vlugter, Waterman, and Van Westen
B-12-H.....	84.0	83	C-30-H.....	98.9	98
B-16-H.....	85.8	86	C-33-H.....	101.2	101
B-19-H.....	87.8	87			
C-1-H.....	82.4	81.5	C-35-H.....	104.0	103.7
C-7-H.....	82.4	84.0	C-37-H.....	105.4	107.0
			C-res-H.....	112.3	112.0
C-13-H.....	84.9	85.5	E-1-H.....	90.4	90
C-20-H.....	90.6	90.0	E-25-H.....	109.1	112
C-26-27-H.....	96.9	95.5			

## VII. CONCLUSION

The data on these completely hydrogenated fractions will be utilized in a subsequent paper to give information as to the chemical composition of the extract portion of the petroleum from which they were derived.

The authors express their gratitude for the advice and encouragement of F. D. Rossini.

## VIII. REFERENCES

- [1] J. C. Vlugter, H. I. Waterman, and H. A. Van Westen, *J. Inst. Petroleum Tech.* **21**, 661 (1935).
- [2] J. Müller and E. Neyman-Pilat, *J. Inst. Petroleum Tech.* **23**, 669 (1937).
- [3] B. J. Mair and C. B. Willingham, *J. Research NBS* **21**, 535 (1938) RP1143.
- [4] Homer Adkins, *Reactions of Hydrogen*, (Univ. Wisconsin Press, 1937).
- [5] R. E. Hersh, E. K. Fisher, and M. R. Fenske, *Ind. Eng. Chem.* **27**, 1441 (1935).
- [6] J. C. Vlugter, H. I. Waterman, and H. A. Van Westen, *J. Inst. Petroleum Tech.* **21**, 701 (1935).
- [7] G. H. Von Fuchs and A. P. Anderson, *Ind. Eng. Chem.* **29**, 319 (1937).
- [8] L. A. Mikeska, *Ind. Eng. Chem.* **28**, 970 (1936).
- [9] L. J. N. van der Hulst, *Rec. trav. chim. Pays-Bas* **54**, 518 (1935).
- [10] B. J. Mair and S. T. Schickltanz, *Ind. Eng. Chem.* **28**, 1446 (1936), *J. Research NBS* **17**, 909 (1936) RP953.
- [11] H. I. Waterman and J. J. Leendertse, *Chimie & industrie* **6**, 59C (1937).
- [12] B. J. Mair and J. D. White, *J. Research NBS* **15**, 51 (1935) RP809.
- [13] C. B. Willingham, *J. Research NBS*. Publication pending.

WASHINGTON, July 21, 1938.